

## MANUFACTURE OF HIGH-DENSITY CERAMIC SINTERS



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16. Abstract  High-d. ceramic sinters are manufd. by coating premolded or presintered porous ceramics with a sealing material of high-SiO <sub>2</sub> porous glass or nitride glass and then sintering by hot isostatic pressing. The ceramics have excellent abrasion and corrosion resistances. Thus, LC-10 (Si <sub>3</sub> N <sub>4</sub> powder) and Y <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> type sintering were mixed and molded to give a premolded porous ceramic (porosity 37%, relative bulk d. 63%) which was dipped in a slurry contg. high-SiO <sub>2</sub> porous glass and an alc. soln. of cellulose acetate to give a coating and dried. The coated ceramic was treated in a N atm. and then sintered by hot isostatic pressing to give a dense ceramic sinter.			
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(54) Manufacturing method of high-density sinters.

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Detailed statement.

Name of the invention: Manufacturing method of high-density ceramic sinters.

Range of the patent application:

1) High-density ceramic sinters are manufactured by coating pre-molded or pre-sintered porous ceramics with a sealing material of high-SiO<sub>2</sub> porous glass or its nitride glass.

Detailed explanation of the invention:

This invention was made on a new manufacturing method of high-density ceramic sinters from porous ceramics using hot isostatic press (HIP).

In recent years there has been much R&D on various ceramic sinters because ceramic is the only material that can be used under severe environments such as high temperature, high vacuum, high stress and high corrosiveness. Particularly, in order to improve thermal efficiency of various heat engines, inlet temperature must be increased considerably and, therefore, high temperature materials with low heat dissipation have been investigated. Since conventional heat-resisting metallic alloys do not have satisfactory thermal and mechanical strength, there has been a growing expectation of ceramics as a material to replace metals. Ceramic is recognized as the material for various die casts or nozzles because of its good abrasion resistance.

To manufacture such ceramic sinters, hot press is usually used. It is difficult to manufacture complex shaped products such as gas turbine blades or mechanical gears, because ceramic raw material is sintered in a rather simply shaped mold. Furthermore, since graphite or aluminum is used for the mold, pressure is limited to several hundred atm which is a large technical limitation to manufacturing ceramic sinters. A new method has been recently proposed utilizing hot isostatic pressing to sinter high density ceramics from pre-molded or pre-sintered ceramics in high temperature and high pressure Argon or Nitrogen gas. Namely, pre-molded or pre-sintered ceramics are enclosed in a high pressure furnace and sintered isotropically under 500-3000 atm of high pressure and 1300-2500°C of high temperature.

Since this HIP method uses Ar or N<sub>2</sub> gas as a pressure medium, the surface of pre-molded or pre-sintered ceramics must be gas-impenetrable. The following three methods have been known in applying HIP on ceramics; 1) Ceramics are pre-molded or pre-sintered up to more than 90% density, or desirably more than 95%, to achieve gas-impenetrability, and then HIP is applied for further densification. 2) If ceramic density is less than 93%, the material is enclosed in a gas-impenetrable capsule, and high temperature and high pressure are applied on the capsule. 3) Instead of a capsule, gas-impenetrable material such as glass is coated on the surface for gas sealing.

However, each of these methods has its drawback. Namely, method 1) requires two steps of sintering at relatively high temperature and, therefore, the final product becomes expensive, limiting this method only to valuable ceramics. Since method 2) needs only one sintering, its product can be less expensive. Yet complex shaped ceramics are difficult to manufacture because a capsule is necessary. Method 3) is the most promising because materials close to the final shape can be used. Presently Pyrex glass, quartz glass or Vycor glass (high-SiO<sub>2</sub> glass) are known as the high pressure gas sealing material. However, these materials are not appropriate for gas sealing of the above mentioned ceramics such as heat engines because more than 1500°C is required to manufacture these ceramics. For example, the viscosity of Pyrex glass is low at high temperatures due to 4% alkali contamination. Although the coating of Pyrex glass onto porous ceramics is simple, penetration of the glass into the pores is significant and the quality of the final ceramic product after HIP process is seriously affected. Quartz glass and Vycor glass have higher viscosity even at high temperatures in contrast to Pyrex glass. It is, however, difficult to use these glasses because crystallization of these glasses starts at around 1200-1300°C, whereas more than 1500°C is necessary to form a glass layer.

We have been investigating new sealing materials which do not have the above drawbacks, and found high-SiO<sub>2</sub> porous glass and its nitride glass as ideal sealing materials. The invention was made of a manufacturing method of high-density ceramic sinters from porous ceramics using HIP characterized by using high SiO<sub>2</sub> porous glass or its nitride as a sealing material.

The high-SiO<sub>2</sub> porous glass becomes glass at the relatively low temperature of 1100-1200°C and has high viscosity as quartz glass. Therefore, a gas impenetrable layer can be easily formed on the ceramic surface and, at the same time the quality of the final product after HIP process will not be affected by sealing because this sealing material does not penetrate into ceramics. HIP can be applied on ceramics as near to the final shape as possible to manufacture high density sinters.

There are no restrictions on pre-molded or pre-sintered porous ceramics as long as II, III, IV group oxide, carbide, nitride or boride is the major component of the ceramics. Pre-molded ceramics made by usual metal molding, rubber press or extrusion, and pre-sintered ceramics made by hot press or normal pressure sintering can be used. There are no restrictions on various binders or sintering aids which are sometimes added during molding or sintering. Porous ceramics with less than 93% density is acceptable and, of course, materials with more than 93% density can be processed without the present invention.

High-SiO<sub>2</sub> porous glass is made from borosilicate glass by separating into Na<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub> phases and SiO<sub>2</sub> phase through thermal treatment and by extracting soluble Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> by acid. Chemical composition of the glass is SiO<sub>2</sub> 94-98%, B<sub>2</sub>O<sub>3</sub> 0.5-5%, Al<sub>2</sub>O<sub>3</sub> 0-2% and Na<sub>2</sub>O 0.01%. Pore size is 40-2000 Å, pore volume 0.3-1cc/g and pore surface area 50-600m<sup>2</sup>/g. This glass has good reactivity with large surface ratio. This material melts into uniform glass at 1000-1200°C.

The above described glass is coated on pre-molded or pre-sintered porous ceramics. The coating method is by dipping in a slurry containing the glass and water or alcohol, or spraying or brushing the slurry. If 0.1-0.2% of cellulose acetate or PVA is added to the slurry, the layer quality after coating can be improved. Thickness of the coating should be about 10μm or desirably more than 100μm. Thickness of more than a mm is not necessary.

When porous ceramics coated with the glass powder are sintered at more than 900°C, or desirably at 1000-1200°C, a gas-impenetrable glass layer is formed on the surface, thus enabling the HIP process. HIP process can be applied in any gas environment. For example, in the air or inert gas, high-SiO<sub>2</sub> glass is formed, and in N<sub>2</sub> or ammonia gas, it becomes its nitride glass. Since these glasses have higher viscosity than quartz glass or Vycor glass, glass penetration into porous ceramics is reduced and a gas-impenetrable seal is formed only on the surface. Since quartz glass has lower reactivity, it does not form nitride glass via the

above mentioned treatment. Instead of coating high-SiO<sub>2</sub> porous glass powder directly, this powder can be made into its nitride first, and this nitride glass powder is coated on the porous ceramic surface. Since the glass sealing and HIP process proceed at the same time, the whole process can be very simplified. Gas-impenetrable glass seal can be made by dipping porous ceramics into powdered high-SiO<sub>2</sub> glass or its nitride glass, and by hot-pressing it at 800-1100°C with a moderate pressure which does not break ceramics.

Table 1 shows melting point temperature and viscosity of major glasses.

ガラス素材 1)	融点 (°C) 2)	高温粘性 (ポイズ) 3)	
		1000 °C	1500°C
パイレックスガラス 4)	820	10 <sup>5.5</sup>	10 <sup>3</sup>
石英ガラス 5)	1650	10 <sup>15</sup>	10 <sup>9</sup>
高ケイ酸質ガラス (バイコール) 6)	1500	10 <sup>12</sup>	10 <sup>7</sup>
窒化物ガラス 7)	-	10 <sup>16</sup>	10 <sup>10</sup>

1) Glass; 2) Melting point; 3) High temperature viscosity; 4) Pyrex glass; 5) Quartz glass; 6) High-SiO<sub>2</sub> glass (Vycor); 7) Nitride glass.

Although there is no particular restriction on HIP conditions, more than 1300°C and 500-3000 atm pressure are recommended.

The nitride glass sealing material made from high-SiO<sub>2</sub> porous glass holds the gas-impenetrability even at HIP condition and has higher viscosity than quartz glass (which loses gas-impenetrability at above 1300°C). It is the best sealing material for HIP treatment of nitride, carbide and boride group ceramics. Furthermore, since sealing is possible for any shape of ceramics, HIP can be applied on materials close to the final products.

Examples and comparisons are described as follows;

Example 1:

Si<sub>4</sub>N<sub>4</sub> powder (Stark LC-10) and Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> type sintering aid (8 wt%)

were mixed and molded via rubber press at 3000 atm pressure. Its relative bulk density was 63% and porosity was 37%. This pre-molded ceramic was dipped in a slurry containing high-SiO<sub>2</sub> porous glass (pore volume 0.3cc/g, average pore radius 150Å, pore surface area 180m<sup>2</sup>/g and average grain radius 0.1mm) and an alcohol solution containing 1% of cellulose-acetate to form 1mm thick layer on the surface. After drying, the coated ceramic was treated in N<sub>2</sub> gas (flow rate 50cc/min) for 30 min at 1200°C. HIP process was applied under the conditions shown in Fig. 1. Final HIP condition was 1800°C, 60 min and 2000 atm pressure in Ar gas. Results are shown in Table 2.

#### Comparison 1:

Porous ceramic as made in Example 1 was coated by quartz glass powder slurry. After treating the material at 1300° for 30 min, HIP process was applied under the same conditions as Example 1. As shown in Table 2, densification is not achieved for this case.

#### Example 2:

SiC powder (Fujimi #8000) was pre-molded by rubber press as described in Example 1. The relative bulk density was 58%. A slurry made from high-SiO<sub>2</sub> porous glass was coated by a brush. After drying, HIP was applied in N<sub>2</sub> gas (flow rate 50cc/min) at 1200° under conditions shown in Fig. 2 . The results are shown in Table 2 together with the results obtained by coating with quartz powder.

#### Example 3:

Si<sub>3</sub>N<sub>4</sub> powder and Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> type sintering aid (12 wt%) were mixed as described in Example 1. After rubber pressing, the material was sintered for one hour under 9.8 atm N<sub>2</sub> gas at 1800°C. The relative bulk density was 91%. One sample was made by coating high-SiO<sub>2</sub> porous glass powder as described in Example 1. Another sample was made by dipping into high-SiO<sub>2</sub> porous glass powder in hot press and pressing for 10 min. at 1000°C and 100kg/cm<sup>2</sup>. These samples were treated by HIP under the same conditions as Example 1. The results are shown in Table 2 together with the results obtained without glass sealing.



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Example 4:

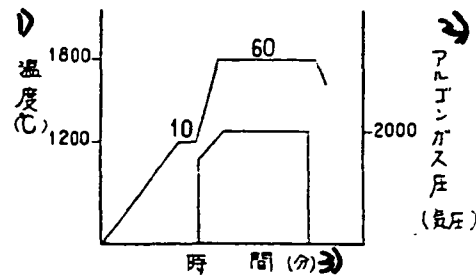
ZrC and ZrB (Cerac) were pre-molded by hot-press for 10 min. at 1600°C and 200kg/cm<sup>2</sup>. The densities were 77% and 83%, respectively. Table 2 shows the results obtained under the same condition as Example 1.

1) Si <sub>3</sub> N <sub>4</sub> 素材	2) 被覆シール材	3) 相対密度 (%)	
		4) HIP 前	5) HIP 後
Si <sub>3</sub> N <sub>4</sub> -8( Y <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> ) 系 (ラバープレス物) 6)	なし 7)	63	61.5
	高ケイ酸質多孔性 ガラス (ドブ漬け) 8)	63	98.2
	石英ガラス (ドブ漬け) 9)	63	62.2
Si <sub>3</sub> N <sub>4</sub> -12( Y <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> ) 系 (反応焼結物) 10)	なし 11)	91	87.5
	高ケイ酸質多孔性 ガラス (ホットプレス) 12)	91	99
SiC	高ケイ酸質多孔性 ガラス (ドブ漬け) 13)	58	96
	石英ガラス (ドブ漬け) 14)	58	58
ZrC	高ケイ酸質多孔性 ガラス (ハケによる塗布) 15)	77	97
ZrB <sub>2</sub>	.	83	99

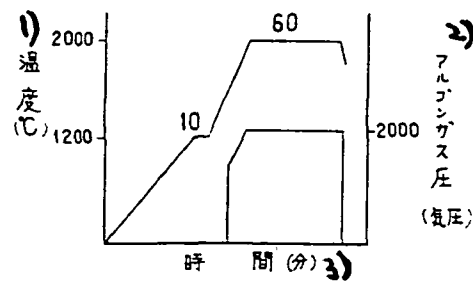
1) Si<sub>3</sub>N<sub>4</sub> raw material; 2) Sealing material; 3) Density; 4) Before HIP; 5) After HIP; 6) Rubber press; 7) Without sealing; 8) High SiO<sub>2</sub> porous glass (dipping); 9) Quartz glass (dipping); 10) (pre-sintered); 11) Without sealing; 12) High SiO<sub>2</sub> porous glass (hot press); 13) High SiO<sub>2</sub> porous glass (dipping); 14) Quartz glass (dipping); 15) High SiO<sub>2</sub> porous glass (brushing).

Fig. 1 HIP schedule for  $\text{Si}_3\text{N}_4$  ceramics.

Fig. 2 HIP schedule for  $\text{SiC}$  ceramics.



第 2 図



1) Temperature; 2) Ar gas pressure (atm.); 3) Time (min.).